

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



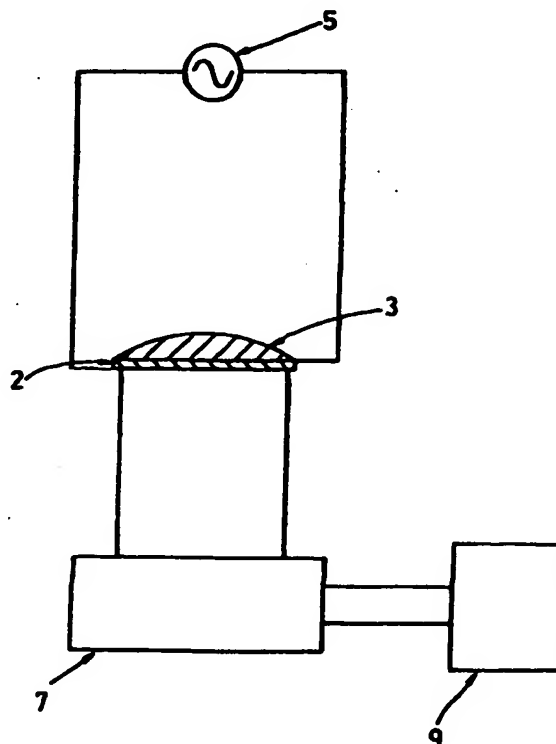
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7: G01N 5/00, 11/16, G01G 3/13		A1	(11) International Publication Number: WO 00/58709
			(43) International Publication Date: 5 October 2000 (05.10.00)
(21) International Application Number: PCT/GB00/01243		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KB, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 30 March 2000 (30.03.00)			
(30) Priority Data: 9907300.9 31 March 1999 (31.03.99) GB			
(71) Applicant (for all designated States except US): BRITISH NUCLEAR FUELS PLC [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): PORT, Simon, Nigel [GB/GB]; 68 Leesands Close, Fulwood, Preston, Lancashire PR2 6GT (GB). JOYCE, Malcolm, John [GB/GB]; 4 Eastview, Fulwood Road, Ribbleson, Preston PR2 6SP (GB). ASH, Dean, Christopher [GB/GB]; Graduate College, Lancaster University, Lancaster LA2 0PC (GB).			
(74) Agent: HARRISON GODDARD FOOTER; Tower House, Merion Way, Leeds LS2 8PA (GB).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: METHOD AND APPARATUS FOR DETERMINING A PHYSICAL OR CHEMICAL CHARACTERISTIC OF A LIQUID

(57) Abstract

A method for determining a physical or chemical characteristic of a liquid in which a drop of the liquid is located on the surface of a crystal of a quartz crystal microbalance. The liquid is evaporated from said surface while a signal output of the crystal microbalance is measured. The signal output is analysed to determine the characteristic of the liquid which may be, for example, the chemical composition or the viscosity. Apparatus for carrying out the method is also provided.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SE	Sweden
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	ME	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**METHOD AND APPARATUS FOR DETERMINING A PHYSICAL OR CHEMICAL CHARACTERISTIC OF A LIQUID**

The present invention relates to the determination of the characteristics of a liquid in particular by using a quartz crystal microbalance (QCM). The characteristics may be, for instance, the chemical composition or the viscosity of the liquid.

5

The QCM was first used as an accurate weight measurement device for measuring the weight of thin film metals. The microbalance works by applying an oscillating electric field across a quartz crystal. The field causes a shear oscillation in the crystal known as the converse piezoelectric effect and the crystal oscillates at a stable resonant frequency. When matter is deposited on the crystal the effective wavelength of the oscillation is increased and the frequency is thus reduced. Therefore, the resonant frequency of the crystal is sensitive to matter deposited on its surface or which is coupled to the surface by viscoelastic means. In addition when connected to a network analyser, admittance, quality factor Q, phase and radio frequency (rf) voltage may be measured. The effect of various interfacial physical phenomena on these quantities has led to the use of the QCM in many analytical applications including adsorption of gases, the solid-liquid function, electrochemistry, thin films, polymers and the study of biological reagents at the crystal surface.

20 The use of the QCM for measurement of fluids has been explored. In comparison with a solid mass, which is entirely mechanically coupled to the quartz surface due to its rigidity, the reduction in resonant frequency in a fluid is due to an effectively rigidly-coupled surface layer. Beyond this layer, the crystal is unaffected by the fluid other than by the small effect of the pressure exerted by the weight of the fluid.

25

As a consequence, analysis of fluids has concentrated on measurement of mass change in a stable liquid layer on the surface of the microbalance. Such a fluid is in equilibrium and can provide a uniform coating across the entire crystal surface. Changes in the composition of the fluid can therefore be determined by measuring the change in mass per unit surface area.

30

According to an aspect of this invention there is provided method for determining a physical or chemical characteristic of a liquid, the method comprising:

depositing said liquid on a surface of a crystal of a quartz microbalance to form a droplet on said surface;

- 5    evaporating said liquid from said surface;  
measuring a signal output of the crystal microbalance; and  
analysing of the signal output to determine said characteristic of said liquid.

The droplet on the surface of the crystal may be described as a sessile body of liquid,  
10    indicating that it simply sits on the crystal surface.

The characteristic of the liquid may be, for instance, some aspect of the chemical composition of the fluid or its viscosity.

- 15    Evaporation of the liquid drop produces changes in a number of measurable physical characteristics of the crystal any of which may be measured as a signal output from the crystal. The measured values are characteristic of the chemical composition of the liquid.

- 20    The droplet preferably has a volume of from 0.5 to 1  $\mu$ l, more preferably about 1  $\mu$ l.

Preferably, the output signal is dependant on the evaporation rate of liquid from the crystal surface.

- 25    Preferably the change in resonant frequency ( $\Delta f_0$ ) is measured. Optionally,  $\Delta f_0$  can be measured by including the crystal microbalance as a component in an oscillator circuit.

- Optionally, any or all of the following physical characteristics, namely, admittance,  
30    quality factor (Q), phase or radio frequency (rf) voltage may be measured.

Preferably the signal is measured as a function of time. Optionally the measurements are taken at least three times per second.

5 Preferably the measurable physical characteristics may be measured using a network analyser.

Preferably the liquid may be composed of a single unknown chemical or a mixture of unknown chemicals. Optionally, the liquid may be an organic liquid. A further option is that the liquid mixture contains at least one organic liquid.

10

Preferably, the signal output is analysed by comparing values derived from the signal output with known values contained in a database. Such a comparison allows the unknown liquid to be identified.

15 The present invention also provides an apparatus for determining a physical or chemical characteristic of a liquid, the apparatus comprising:

a quartz crystal microbalance;

means for depositing said liquid on the surface of said crystal microbalance to form a droplet on said surface;

20 means for causing the evaporation of said liquid on the surface of said surface;

means for measuring the signal output of the crystal microbalance; and

means for analysing the signal output to determine a said characteristic of said liquid.

25 For many volatile liquids the observed frequency response is qualitatively characteristic of the specific liquid used such that a non-deterministic recognition method can be employed in order to identify the liquid. The origin behind such characteristics is believed to be the variety interaction between convection and conduction processes, and the surface tension of the liquid. Such liquids can be termed *unstable-interface* liquids. However, for other, *stable-interface* liquids, the responses are generic, differing only in the severity of the response curve. The  
30 response curve is parameterised by the crystal sensitivity  $S(r, \phi)$ , where  $r$  is the radius

and  $\phi$  is the angle subtended from the crystal centre across its surface. This sensitivity is formally expressed as a series of Bessel functions but is more often approximated as Gaussian, as in equation (1):

$$5 \quad S(r, \phi) = S_0 \exp\left(-\beta(\phi) \frac{r^2}{r_e^2}\right) \quad (1)$$

where  $\beta$  controls the sensitivity dependence on radius  $r$  and the radius of the QCM electrode is  $r_e$ . It is possible to relate  $\Delta f(t)$  to elapsed time  $\Delta t$  as provided in the linear expression of equation (2):

$$10 \quad \Delta f(t) - \frac{\Delta f_{\max}}{(1 - \exp - \beta)} = -\frac{\Delta f_{\max}}{(1 - \exp - \beta)} \exp - \beta \left( \frac{r^2(t_0)}{r_e^2} + \frac{v_r \Delta t}{\pi r_e^2} \right) \quad (2)$$

where  $\Delta f_{\max}$  is the maximum change of frequency observed,  $r(t_0)$  is the radius of the drop at the moment it is deposited and  $v_r$  is the *retreat speed*. By dividing through by  $-\Delta f/(1 - \exp - \beta)$  and taking logarithms:

$$15 \quad -\ln \left[ 1 - \Delta f(t) \frac{(1 - \exp - \beta)}{\Delta f_{\max}} \right] = C_1 + C_2 \Delta t \quad (3)$$

where:

20

$$C_1 = \beta \left( \frac{r(t_0)}{r_e} \right)^2$$

$$C_2 = \beta \frac{v_r}{\pi r_e^2}$$

25 where  $v_r$  is defined in terms of area change per unit time,  $\text{m}^2\text{s}^{-1}$ .

Preferably a computer is used to store a database of known values. Preferably a computer is used to compare the known and unknown values and select the best fit from the known signals to determine the identity of the unknown chemical.

- 5 Preferably the crystal is driven at its resonant frequency or harmonics thereof by an Alternating Current supply. Preferably the crystal microbalance is constructed from quartz crystal. Preferably the quartz crystal is unpolished. Optionally the quartz crystal has a diameter of between 5mm and 15mm.
- 10 Preferably the quartz crystal microbalance is attached to a network analyser by means of an electrode on both its upper and lower surfaces.

- Preferably the rate of evaporation is controllable. Preferably the rate of evaporation is controlled by controlling the temperature of the crystal surface. Optionally, the rate
- 15 of evaporation is controllable by controlling the pressure at the crystal surface.

Preferably, the volume of liquid deposited on the surface can be controlled.

- The method of the present invention can be used to determine the viscosity of the
- 20 liquid droplet. From the Sauerbrey equation we know that the change in oscillating frequency of a Quartz crystal microbalance transducer is related to the mass loading that crystals surface (equation (1)).

$$\Delta f = \frac{-2f_o^2 \Delta m}{A\sqrt{\mu_q \rho_q}} \quad (1)$$

30

$\Delta f$ = frequency change,  $f_o$ = crystal resonant frequency,  $\Delta m$ = mass change,  $A$ = electrode area,  $\mu_q$ = shear modulus of quartz and  $\rho_q$ = density of quartz.

When a droplet is in contact with an oscillating surface, the oscillations passing from the surface into the fluid droplet decay according to an exponential law. The penetration depth  $\delta$  is a distance normal to the crystal surface over which the amplitude of the oscillations reduces by  $e$  times. This penetration depth is dependent  
 5 on the properties of the fluid forming the droplet as seen in equation (2).

$$\delta = \left( \frac{\eta}{\pi f \rho_1} \right)^{\frac{1}{2}} \quad (2)$$

15 where: -  $\eta$  = absolute fluid viscosity, and  $\rho_1$  = fluid density.

The Sauerbrey equation assumes a solid mass loading of the crystal where the whole of the mass oscillates with the crystal frequency. As explained above, when the loading is fluid, the whole volume of the droplet will not oscillate with the crystal as  
 20 the amplitude decays through the fluid. The volume of fluid oscillating at the crystal frequency is equal to a volume of  $A \cdot \delta / 2$ . This means it can be assumed that a layer forms on the electrode, which acts as a solid mass and is known as the rigidly coupled layer. This layer is the  $\Delta m$  responsible for the frequency change observed in the crystal oscillations. The mass of this layer is related to the density and volume of  
 25 the droplet as shown in equation (3).

$$\Delta m = \rho_1 A \frac{\delta}{2} \quad (3)$$

Substituting equations (2) and (3) into equation (1) gives an equation relating  
 35 frequency change to viscosity.

$$\Delta f = -f_o^{\frac{1}{2}} \sqrt{\frac{\rho_1 \eta_1}{\pi \mu_1 \rho_1}} \quad (4)$$

This rearranges for viscosity as shown in equation (5)

$$\eta_l = \frac{\Delta f^2 \pi \mu_q \rho_q}{f_o^3 \rho_l} \quad (5)$$

5

The invention will now be described by way of example with reference to the accompanying drawings of which:

Figure 1 shows the equipment and experimental set up used for measuring liquid characteristics on evaporation;

10

Figure 2 shows a set of graphs for plotting the change in resonant frequency of the crystal against time for a range of liquids on evaporation;

Figure 3 shows a set of graphs plotting the change in resonant frequency against time for a liquid using different types of crystal;

Figure 4 shows a schematic diagram of a device for determining the content of a liquid;

15

Figure 5 is a graph showing the change in resonant frequency against time for butan-1-ol;

Figure 6 shows response curves for a range of alcohols; and

20

Figure 7 shows the results of viscosity measurements on TBP/OK mixtures.

Referring to Figure 1, a quartz crystal was used and operated at a resonant frequency of 10MHz by frequency generator 5. The quartz was unpolished, with total diameter of 8mm and a silver electrode of approximately 4mm diameter on each face. The crystals were connected to a network analyser 7 using grounded coaxial leads to minimise stray capacitance effects and external interference. The crystal surfaces were orientated in the horizontal plane. The network analyser 7 used in this work was a Hewlett Packard 8753C and was interfaced to a personal computer 9 via Lab View, a data acquisition software package. The network analyser 7 was set up to record the change in frequency  $\Delta f$  from the resonant frequency  $f_o$  at a rate of 3 measurements per second.

25

30

In performing the experiment a droplet of alcohol 3 was applied to upper surface of the crystal 2 using a syringe (not shown). The droplet was observed to completely

cover the upper surface 2 of the crystal and a mean droplet volume of 1mm was recorded. Data were recorded from a time immediately prior to the droplet being deposited on the upper surface of the crystal 2 to immediately after  $\Delta f$  had returned to zero.

5

A selection of volatile alcohols were used in the experiments to study the effect of increasing molecular chain length on  $\Delta f$  over time.

The above experiment examined methanol, ethanol, propan-2-ol, butan-1-ol and pentan-1-ol.

10

Figure 2 shows the change in resonant frequency of  $\Delta f(\text{Hz})$  against time for each of the above alcohols. 2 The plots (a) to (e) show the results for methanol, ethanol, propan-2-ol, butan-1-ol and pentan-1-ol, respectively.

15

In general, the response of the oscillating quartz crystal to the dynamic loading of the evaporating alcohol is a negative pulse with a period of several minutes. Although a similar general response is exhibited by all give alcohols, each response has specific aspects that are characteristic of the alcohol used.

20

Figure 3 shows the change in resonant frequency  $\Delta f(\text{Hz})$  against time(s) for ethanol on three separate crystals of the same type.

25

Although there are changes in the width of response due to variations in droplet size volume, which result in changes in the length of time for evaporation to occur, the characteristic shape of response is reproduced. This was evident for the other alcohol samples used.

30

In Figure 4 a device 31 is shown which can be used to determine the chemical contents of a sample. A sample 32 is placed on the upper surface of a quartz crystal 39 by means of a syringe or other accurate measuring device. Use of such an

accurate measuring device ensures that a substantially constant volume of sample 32 can be analysed. Temperature control elements 35 are used in conjunction with a thermometer (not shown) in order to control the temperature inside the evaporation chamber 33. This in turn controls the rate of evaporation for the sample. As in  
5 example 1, the crystal is driven by an ac signal generator 49 at the resonant frequency of the crystal (or harmonics thereof).

On evaporation, the change in frequency  $\Delta f$  is sampled by a network analyser 41 which is set to sample  $\Delta f$  3 times per second. Sampling rate can be easily increased  
10 to improve accuracy. The data obtained during sampling is then stored in a memory chip 43. Once all of the data has been collected, the stored data is downloaded onto a computer where analysis of the data is undertaken.

Figure 5 shows the change in resonant frequency  $\Delta f$  (Hz) against time (t) for butan-1-  
15 ol with a least squares fit to the region where the evaporation rate is constant. This linear region of the graph is due to the increase in evaporation rate being compensated for by a decrease in mass on the crystal surface. After the linear section the change in mass dominates. Figure 5 has a characteristic shape similar to that of a fermi function.

20 Data analysis can be performed by using equation (3) set out above. The value of the constant  $\beta$  has been taken to be  $2.00 \pm 0.05$  and independent of  $\phi$ , which is consistent with other studies of radial sensitivity of quartz crystals. Plots of  $y = -\ln(\Delta f(t)(1 - \exp(-\beta) / \Delta f_{\infty} - 1))$  against  $\Delta t$  for the series of alcohols studied are  
25 presented in Figure 6. The alcohols are a) methanol, b) ethanol, c) propan-2-ol, d) butan-1-ol and e) pentan-1-ol.

The data of Figure 6 are the quasi-linear regions of the complete data sets. In all cases, both the early data ( $t < 100$ s), and that just prior to the crystal reaching  $\Delta f = 0$  Hz,  
30 exhibit variations from the central linearity which is characteristic of radial sensitivity effects currently beyond the model used. Indeed, for methanol the linear

feature between these non-linear aspects is very short due to the rapid evaporation of this alcohol.

The region of each data set presented in Figure 6 has been fitted using a linear regression in order to extract the radial retreat speed  $v_r$ . These results are presented in Table 1:

Alcohol	Methanol	Ethanol	Propanol	Butanol	Pentanol
Region of fit	95-105s	96-99s	60-80s	100-200s	300-500s
Degrees of freedom	29	8	59	299	599
$R^2$	0.94	0.964	0.994	0.988	0.953
Slope / $10^{-2} \text{ s}^{-1}$	$1.16 \pm 0.05$	$9.68 \pm 0.66$	$2.22 \pm 0.02$	$0.465 \pm 0.003$	$0.231 \pm 0.002$
Constant	$-1.71 \pm 0.05$	$-9.77 \pm 0.64$	$-1.99 \pm 0.02$	$-1.082 \pm 0.005$	$-1.353 \pm 0.009$
$v_r / 10^{-7} \text{ m}^2 \text{ s}^{-1}$	$4.56 \pm 0.20$	$38.01 \pm 2.59$	$8.72 \pm 0.08$	$1.83 \pm 0.01$	$0.907 \pm 0.008$

TABLE. 1. Results from the linear regression analysis of the data in Figure 6.

10

In summary, a quantitative method of fluid identification is possible, in addition to the response recognition method, *via* the retreat speed  $v_r$ . This is particularly advantageous in those cases where the frequency responses are characteristically similar, for example those of butanol and pentanol in the data provided here.

15

In cases where the liquid is unknown, the data available from measurement of the change in resonant frequency with evaporation rate can be correlated to a library of known values. The measurements can be subjected to signal processing, for instance, by Fast Fourier transformation.

20

A further example of use of the above technique is for the analysis of samples of the extractant tri-butyl phosphate (TBP). Despite being chemically stable TBP undergoes some thermal and radiolytic degradation in the process of uranium

extraction to form di-butyl phosphate and mono-butyl phosphate. Di-butyl phosphate forms strong extractable complexes with plutonium and zirconium, whilst mono-butyl phosphate tends to form precipitates. Both products lead to complications in the extraction process and are removed by washing the solvent with alkali. Therefore the purity of TBP must be accurately monitored to determine the point at which washing is required.

As a further example, the method of the present invention may be used to measure viscosity and the viscosity values may be used to determine the percentage of odourless kerosene (OK) in TBP. The measured viscosity is largely independent of the crystal used and of the droplet size. Four experiments were conducted, each with a different crystal and with no particular control of droplet size. The "actual" viscosity was also measured using a reverse flow viscometer in a constant temperature water bath.

15

The results are shown in Figure 7. A clear difference in measured viscosity is obtained as the percentage of OK increases. Measurement of viscosity by the method of the present invention can be used as a technique to give a rapid indication as to whether this TBP/OK solvent system is going "out of specification" during its use in, for instance, nuclear fuel treatment processes.

20

## CLAIMS

1. A method for determining a physical or chemical characteristic of a liquid, the method comprising:  
5 depositing said liquid on a surface of a crystal of a quartz crystal microbalance to form a droplet on said surface;  
evaporating said liquid from said surface;  
measuring a signal output of the crystal microbalance; and  
analysing the signal output to determine said characteristic of said liquid.  
10
2. A method according to Claim 1 wherein the liquid characteristic is the chemical composition of said liquid.
3. A method according to Claim 1 wherein the liquid characteristic is the  
15 viscosity of said liquid.
4. A method according to any of the preceding claims, wherein said liquid is comprised of a single unknown chemical or a mixture of unknown chemicals.
- 20 5. A method according to any of the preceding claims wherein the liquid comprises an organic liquid.
6. A method according to any of the preceding claims, wherein said droplet has a volume of from 0.5 to 1  $\mu$ l.
- 25 7. A method according to Claim 6, wherein the volume of the droplet is about 1  $\mu$ l.
8. A method according to any one of the preceding claims, wherein the signal  
30 output is one dependant on the evaporation rate of liquid from the crystal surface.

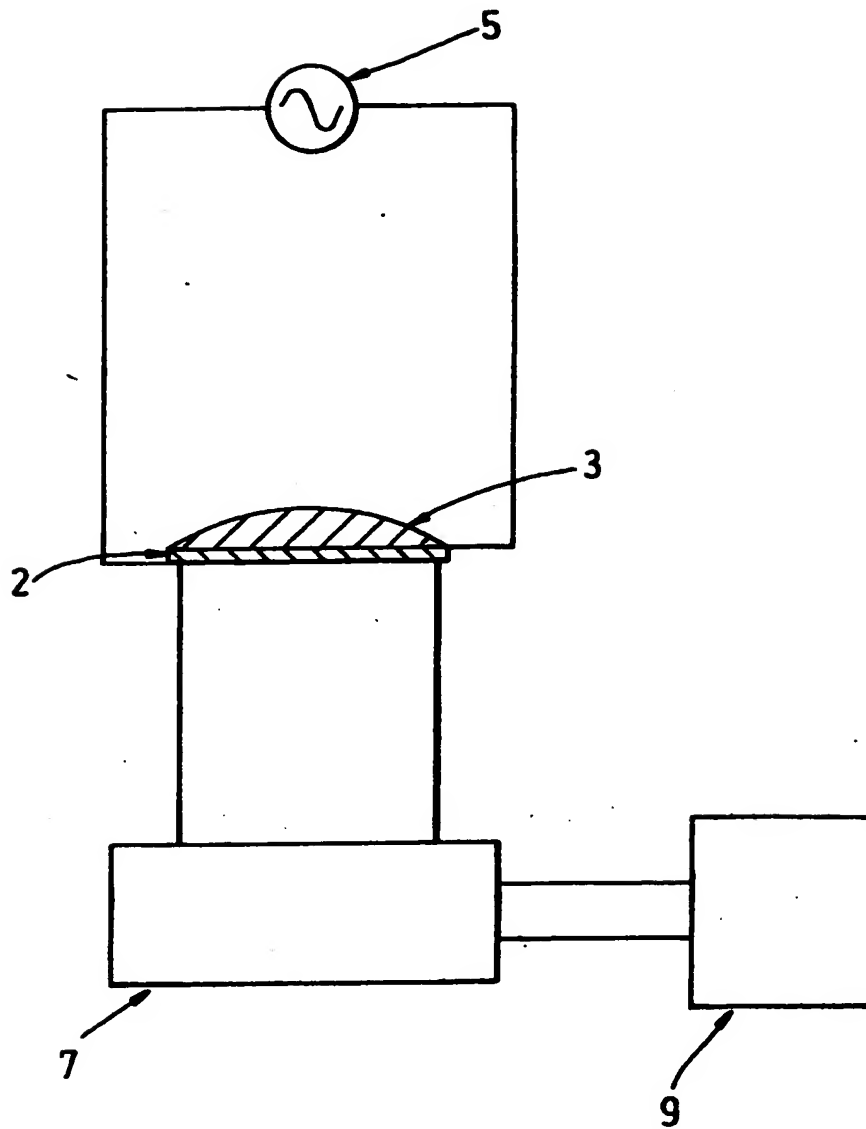
9. A method according to any one of the preceding claims, wherein the signal output gives information on at least one physical property of the crystal microbalance.
- 5
10. A method according to Claim 9, wherein the at least one physical property is selected from the resonant frequency, the admittance, the quality factor, the radiofrequency voltage and the phase.
- 10 11. A method according to any of the preceding claims, wherein the signal output is analysed by comparing values derived from the signal output with known values contained in a database.
12. A method according to Claim 11, wherein the values derived from the measured values are obtained from equation (3) as herein set out and defined.
- 15
13. A method according to any of the preceding claims, wherein the rate of evaporation is controllable.
- 20 14. A method according to any of the preceding claims, wherein the rate of evaporation is controlled by varying the temperature at the crystal surface.
15. A method according to any of the preceding claims, wherein the rate of evaporation is controlled by varying the pressure at the crystal surface.
- 25
16. An apparatus for determining the chemical composition of a liquid, the apparatus comprising:  
a quartz crystal microbalance;  
means for depositing said liquid on the surface of a crystal of said crystal microbalance to form a droplet on said surface.  
30 means for causing the evaporation of said liquid from said surface;

means for measuring the signal output of the crystal microbalance; and  
means for analysing the signal output to determine a fluid characteristic of  
said liquid.

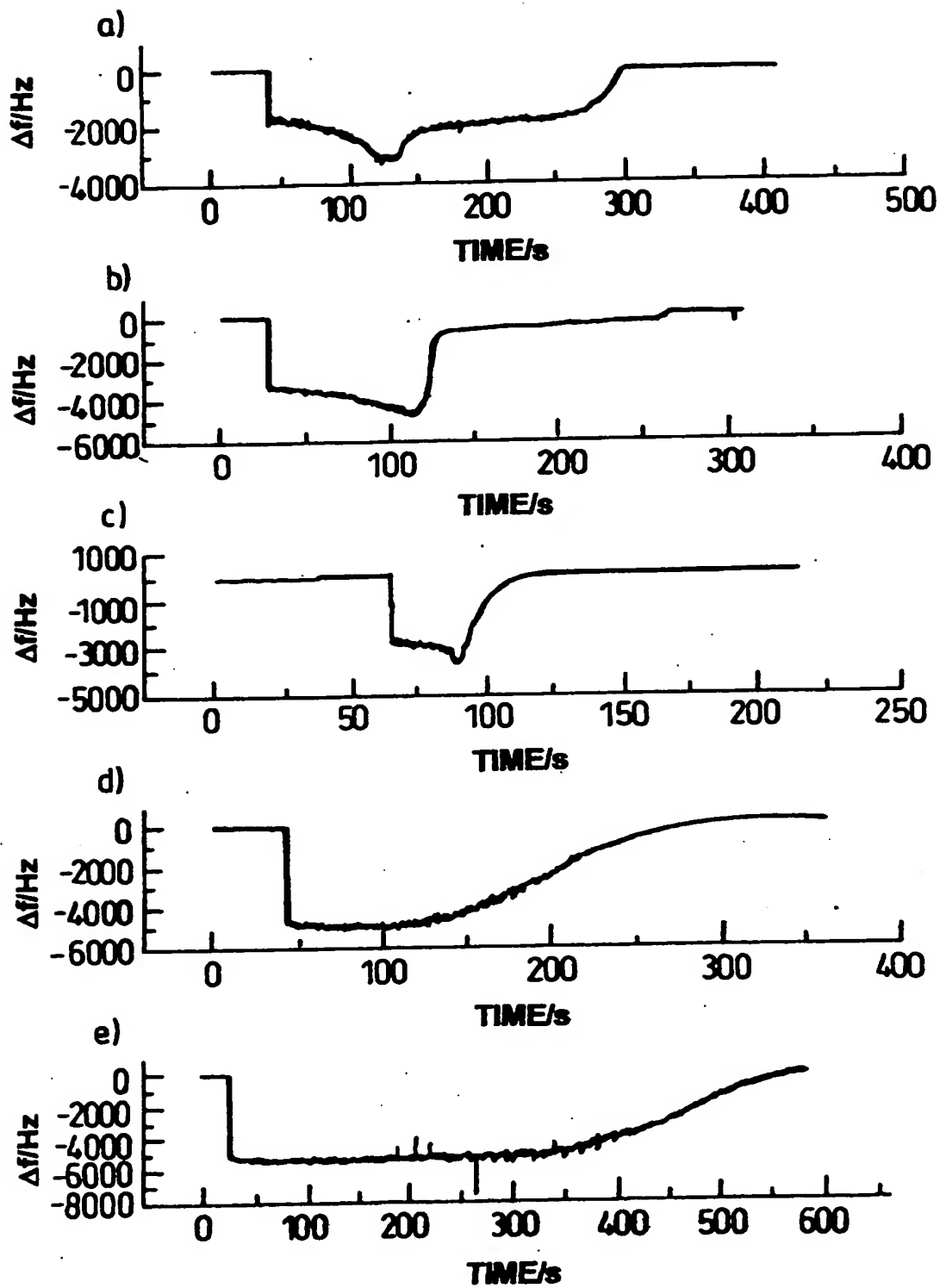
5

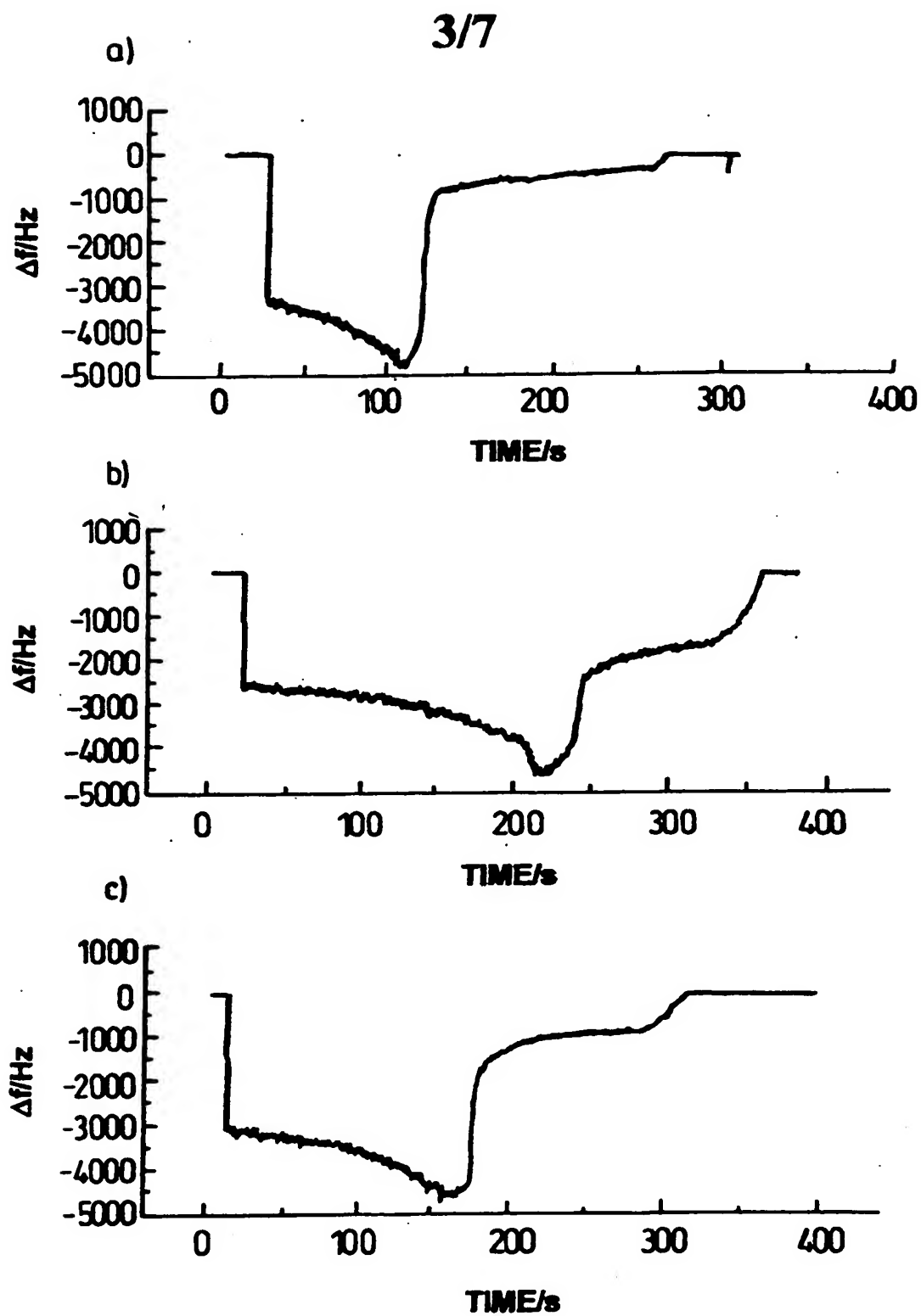
10

1/7

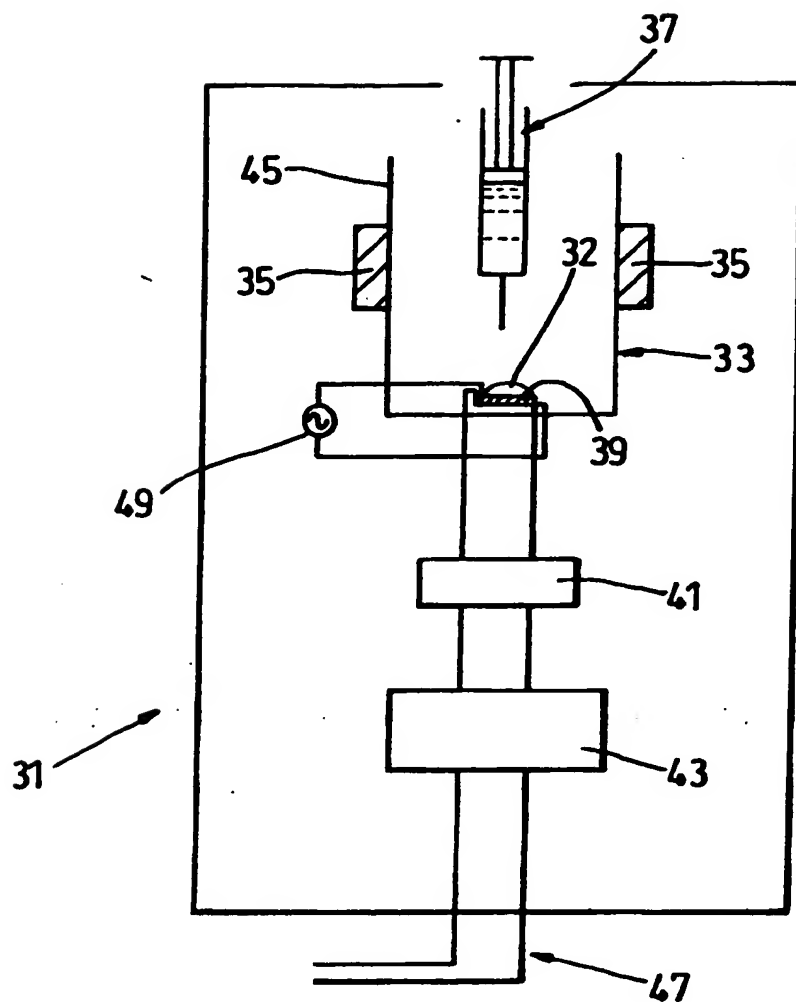
*Fig. 1*

2/7

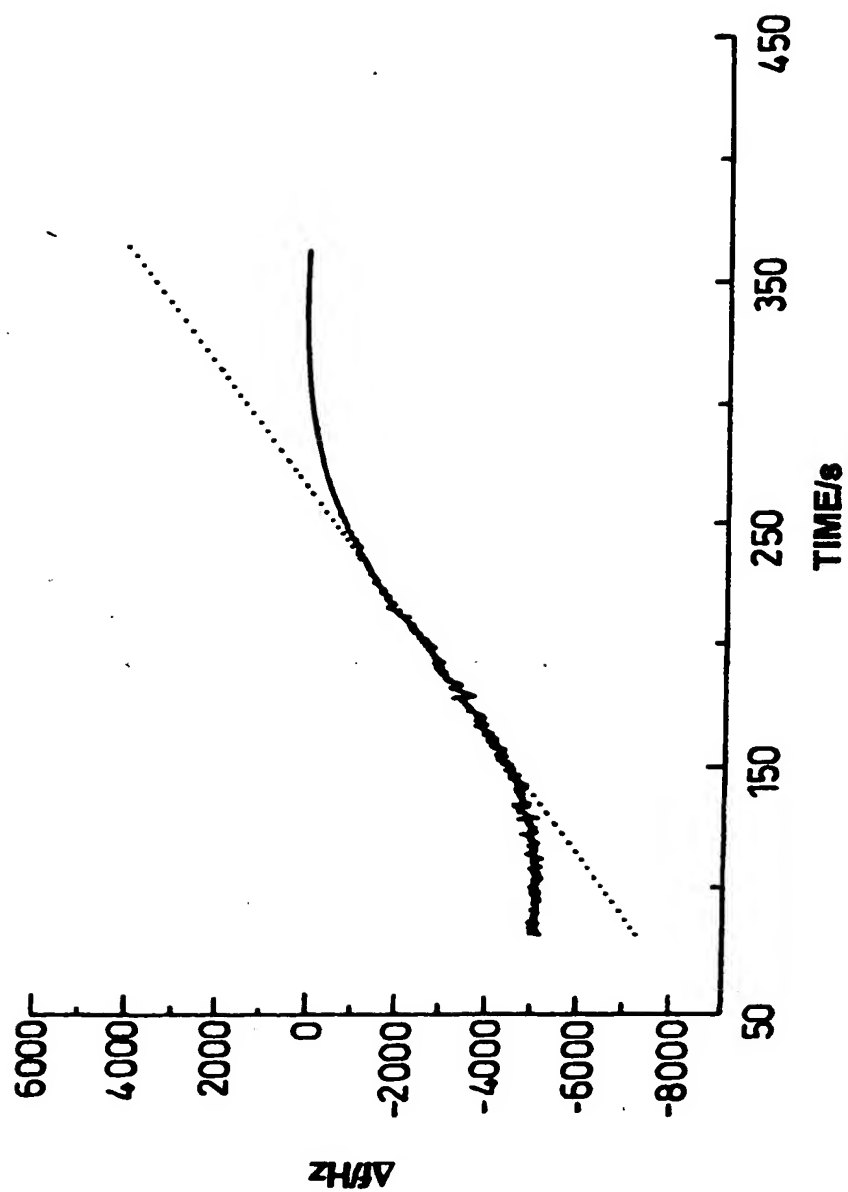
**Fig. 2**

**Fig. 3**

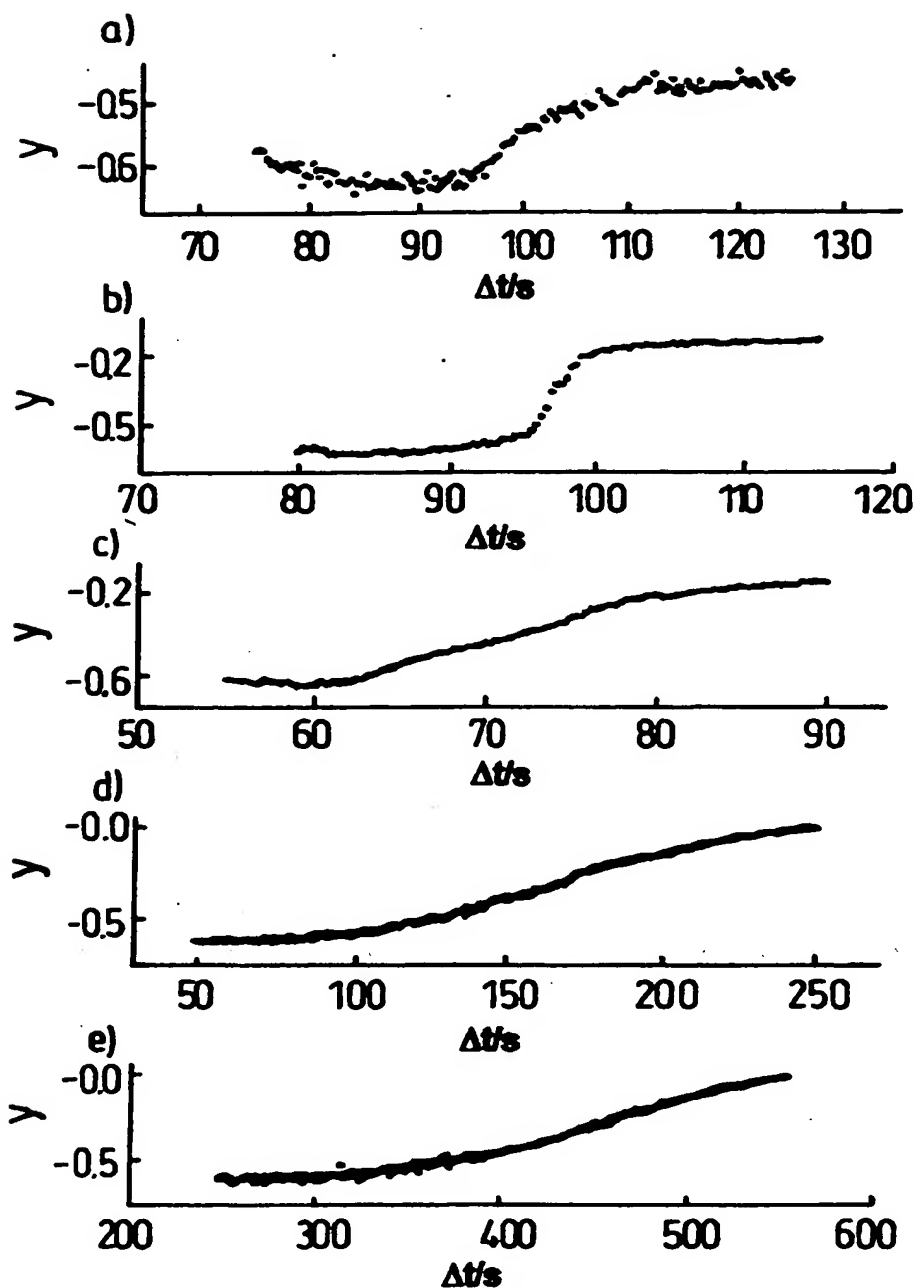
4/7

*Fig. 4*

5/7

*Fig. 5*

6/7



Plot of  $y = -\ln(1 - (\Delta f / \Delta f_{max}) (1 - \exp(-\beta)))$  against elapsed time  $\Delta t$  for methanol (a), ethanol (b), propan-2-ol (c), butan-1-ol (d), and pentan-1-ol (e).

**Fig. 6**

7/7

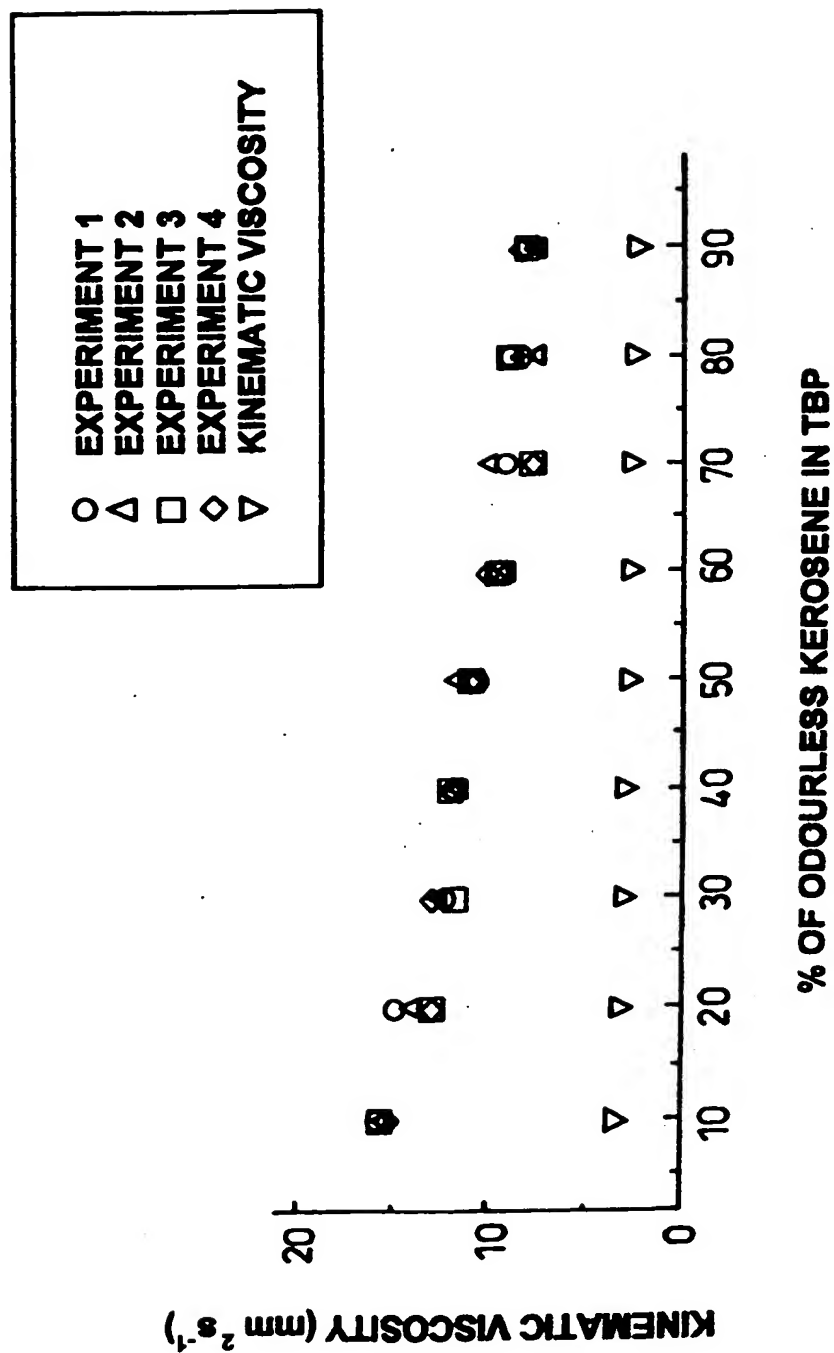


Fig. 7

# INTERNATIONAL SEARCH REPORT

International Application No.  
PC ..GB 00/01243

**A. CLASSIFICATION OF SUBJECT MATTER**  
G01N5/00,G01N11/16,G01G3/13

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
G01G,G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5734098 A (R. KRAUS) 31 March 1998, abstract, -claims. ---	1, 3, 5, 16
A	US 4788466 A (D.W. PAUL) 29 November 1988, abstract, column 1, lines 5-39, claims, fig. 2. ---	1, 16
A	US 5112642 A (A. WAJID) 12 May 1992, abstract, claims, fig. 1. ---	1, 16
A	WO 98/39648 A (ALPHA M.O.S.) 11 September 1998, abstract, claims, fig. 1. ---	1, 2, 16
A	WO 96/35103A ---	1, 16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- A- document defining the general state of the art which is not considered to be of particular relevance
- E- earlier document but published on or after the international filing date
- L- document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- O- document referring to an oral disclosure, use, exhibition or other means
- P- document published prior to the international filing date but later than the priority date claimed

- T- later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- X- document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- Y- document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- Z- document member of the same patent family

Date of the actual completion of the international search  
13 June 2000

Date of mailing of the international search report  
21.07.00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 631 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer  
ERBER

# INTERNATIONAL SEARCH REPORT

- 2 -  
PCT/GB 00/01243

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>(M. RODAHL ET AL.) 07 November 1996, abstract, claims, fig. -----</p>	

**ANHANG**

Zum internationalen Rechts...anbe-  
richt über die internationale Patent-  
anmeldung Nr.

In diesem Anhang sind die Mitglieder der  
Patentfamilien der im obengenannten  
internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur  
Unterrichtung und erfolgen ohne Gewähr.

**ANNEX**

To the International Search  
Report to the International Patent  
Application No.

**PCT/GB 00/01243 SAE 274679**

This annex lists the patent family members  
relating to the patent documents cited in the  
above-mentioned search report.  
The European Patent Office is in no way  
liable for these particulars which are merely  
given for the purpose of information.

**ANNEXE**

Au rapport de recherche inter-  
national relatif à la demande de  
brevet international n°

La présente annexe indique les membres de  
la famille de brevets relatifs aux documents  
de brevets cités dans le rapport de  
recherche international visé ci-dessus. Les  
renseignements fournis sont destinés à titre  
indicatif et n'engagent pas la responsabilité  
de l'Office.

Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 5734098	31-03-1998	AU A1 25877/97	17-10-1997
		AU B2 718367	13-04-2000
		BR A 9702225	23-02-1999
		CA AA 2222046	02-10-1997
		CN A 1188546	22-07-1998
		EP A1 829010	18-03-1998
		JP T2 11508054	13-07-1999
		NO A0 975376	24-11-1997
		NO A 975376	23-01-1998
		WO A1 9736178	02-10-1997
US A 4788466	29-11-1988	none	
US A 5112642	12-05-1992	DE A1 4035240	02-10-1991
		DE C2 4035240	15-10-1998
		GB A0 9021531	14-11-1990
		GB A1 2242523	02-10-1991
		GB B2 2242523	27-10-1993
		JP A2 3285108	16-12-1991
		JP B2 2974253	10-11-1999
WO A1 9839648	11-09-1998	FR A1 2760533	11-09-1998
		FR B1 2760533	28-05-1999
WO A1 9635103	07-11-1996	AU A1 57837/96	21-11-1996
WO C2 9635103	10-02-2000	EP A1 775295	28-05-1997
		SE A0 9501653	04-05-1995
		SE A 9501653	05-11-1996
		SE C2 504199	02-12-1996
		US A 6006589	28-12-1999

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**